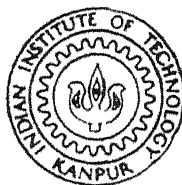


ELECTRODEPOSITION OF Cr-WC COMPOSITE COATINGS

by

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A Thesis Submitted
in Partial Fulfilment of the Requirements
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D. PRABHAKARAN

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CERTIFICATE

This is to certify that the report entitled
' Electrodeposition of Cr-WC Composite Coatings '
Submitted by D. PRABHAKARAN in partial fulfilment of
the requirements for the Degree of Master of Technology
has been carried out under my supervision and has not
been submitted elsewhere for a degree.

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ABSTRACT

Electrodeposited composite coatings of Cr-WC have been produced by keeping WC particles in suspension using magnetic stirrer in a bath containing chromic acid and sulphuric acid in a ratio of 100:1. The effects of WC content in the bath and current density, on the WC content in the coating and on cathode current efficiency have been studied. The two stage adsorption mechanism proposed by Guglielmi is also applicable in this system and the second stage of adsorption was found to be the rate controlling step.

CHAPTER-I

INTRODUCTION

Chromium electrodeposits are primarily used to increase the service life of functional parts by increasing their resistance to wear, abrasion, corrosion and oxidation. Electrodeposited chromium coatings would find many more application in engineering industries if we somehow either increase their hardness or decrease their coefficient of friction.

The development of composite materials reveal that the property of the single composite system possess both extended physical and mechanical property of the combined materials. Therefore, if we somehow embed hard particles in electrodeposited chromium coatings, it will increase the hardness and hence the wear resistance property or if we embed particles with low shear stress then we can decrease the coefficient of friction of the coatings.

The ideas of composite materials gave rise to the development of electrodeposited composite coatings. Earlier literature review shows that electrodeposited composite coatings for Ni, Cu, Ag etc. as matrix was possible (1). But it was difficult to obtain composite coatings with

chromium matrix. However, recent work at I.I.T. Kanpur (2,2a) has shown that it is possible to codeposit both hard and self lubricating particles in a chromium matrix. Effect of bath and operating variables on the amount of graphite and Al_2O_3 codeposited with chromium had been studied in detail (2, 2b).

Tungsten carbide particles are very hard and stable at high temperature. So the codeposition of WC with chromium can be used in highly abrasive conditions at high temperatures. The feasibility of electrodeposition of Cr-WC composite coating was shown by Raj Narayan and Surjit Singh (2a). The present study was undertaken to study the different operating and bath variables on the cathode current efficiency and the amount of WC codeposited with chromium. The underlying mechanism which controls electrodeposition of Cr-WC coatings had also been studied.

CHAPTER -II

LITERATURE REVIEW

2.1 PRODUCTION OF ELECTRODEPOSITION OF COMPOSITE COATINGS:

Electro deposition of composite coatings are produced by suspending the second phase particles, in the form of fine powder or filament, in the conventional plating electrolyte. Two type of metallic matrices being possible namely pure metal and alloy type. Besides the choice of the metallic matrix, consideration has to be given to the choice of second phase which can be a powder or a fibre, with further distinction between conducting and non-conducting particles. Moreover, fibres can be embedded perpendicular to each other or it can be randomly oriented.

Depending on the type of inert particles chosen, the properties and the applicability of the product may be different. In connection with the choice of second phase there are three limitations :

- (i) The second phase particles has to be available in powder or fibre form .
- (ii) It has to be wetted by the solution.
- (iii) It should not be soluble in the plating bath.

Depending upon the intended application, composite coatings could be catagorised into the following:

- (i) Dry lubricant coatings.
- (ii) Wear resistant coatings.

- (iii) Heat treatable metal alloy coatings
- (iv) Nuclear control coatings.
- (v) Corrosion and oxidation resistance coatings.

2.2 DRY LUBRICANT COATINGS:

Instead of hard particles, if soft particles having low shear strength are dispersed in metal matrix, then the resulting composite coating may be expected to possess good antifriction properties. Various particles codeposited with metal to produce drylubricant composite coatings are MoS_2 , graphite and BaSO_4 . Ni- MoS_2 composite have been reported by various investigators (3-7). Vast and Bazzarre (3) codeposited MoS_2 with Ni from sulphamate bath. pH was found to have a pronounced effect on the codeposition. Increase in pH decrease the volume percentage of MoS_2 . The adhesion of coating decreases with increase in MoS_2 in the coating (3,5,7). The internal stress in the composite coating was less than that in nickel coatings. The coefficient of friction of the composite coating was between 0.05-0.18 (3). Young (8) described the codeposition of MoS_2 with chromium. Deposits from bath containing MoS_2 were very poor and after two or three runs, the bath became incapable of producing continuous chromium deposits.

2.3 CORROSION AND OXIDATION RESISTANT COATINGS:

The well known application of codeposition to improve the corrosion resistance of coatings is the production of microporous chromium layers by codeposition of non conducting particles in the underlying Ni layer. Corrosion of Ni will thus occur over an increased surface resulting in a small depth of attack. Other examples are Cr-ZrC coating which offer good resistance to sulphur corrosion. In an oxygen enriched atmosphere Ni-Al₂O₃ composite coatings have better oxidation resistance than plain nickel coating and good results are also reported for electrodeposited Ni-SiC composites by Stott and Ashby (9). The introduction of fine siliconcarbide particles causes a significant decrease in oxidation rate, largely due to internal oxide derived particles acting as barriers to Ni³⁺ diffusion through the NiO scale. A recent report on the oxidation behavior of cobalt-chromium carbide electrodeposits (10) confirms that the movement of oxygen through oxidation scales is a significant factor in the oxidation characteristics of these composites. It was shown that the oxidation resistance of electrodeposited cobalt-chromium carbide composite coatings can be significantly increased by first carrying out an inert atmosphere heat treatment to produce homogeneous alloy. Due to complexity of corrosion and oxidation environments it is difficult at present

to give a rational explanation of these various observations and performance tests are required for each new application.

2.4 WEAR RESISTANT COATINGS:

Many investigators believe that the wear resistance of composite coatings was largely governed by the wear properties of the hard particles, provided the wear load was less than the compressive yield strength of the matrix material. It was thought that when a composite coating having hard particles dispersed in it, ~~be~~ brought in contact with a sliding counterface the wear continues till the hard particles are exposed so that they bear the wear load. With this assumption many investigators tried to codeposit hard particles like Al_2O_3 , TiO_2 , SiC , Cr_3C_2 , TiC , diamond etc. in the range of metal matrix such as Ni , Cr , Co etc. (11).

It was found that in Ni matrix most of the fine oxide particles can be codeposited easily using the conventional watts/sulphamate bath. Ramanaskene (12) successfully codeposited particles of SiO_2 , Al_2O_3 with Ni from watts-type solution. However, the concentration of solid particles in the Nickel deposit was low upto 1 wt.pct. SiO_2 and upto 4 wt. pct. Al_2O_3 . Malone (13) studied the Ni-ThO_2 in both the sulphamic and watts type electrolyte and showed that electrodeposition can be successfully

employed to produce dispersion strengthened materials. M.M. Ristic and M.K. Pavicevic (14) investigated the bond between Al and Ni in Al_2O_3 - Ni system and found that it can be either ionic-covalent or a metallic one. The electronic structure of the interatomic bond was very similar to Ni_2Al_3 alloy type but was not identical with it. This will be useful in understanding the fundamental aspects of the structure of the composite coating system which in turn will be helpful in predicting the bond strength of the second phase particles with the metal matrix.

R.S. Sayfullin, I.M. Valeyev and I.A. Addullin (15) produced Ni composite coatings at non-stationary parameters of electrolysis. They found that the cleanliness of composite electro-chemical coatings (CEC) and the uniformity of the second phase distribution increased with the increasing amplitude of anode. The use of non stationary electrolysis enabled the range of CEC physical properties to be widened. R. Suchentiunk (16) produced dense, homogeneous and pore-free composite by embedding high strength fibres like Boron carbide coated boron fibres in electrodeposited metal (Cu, Al, Ni). This technology was utilized in producing pressure vessels for space application.

R.S. Sayfullin, I. Ekkart and N.V. Bortunov(17) were able to produce Al-alumina coatings of any thickness from a bath containing equal parts of AlCl_3 and LiAlH_4 in tetrahydrofuran solutions plus dispersed corundum particles. They found that the microhardness of the coating can be as high as 1310 MPa for a coating containing 19% Al_2O_3 . Also they found that the cathode and anode yields of Al were approximately 100%. Their deposition rate was 12 μm per hour at a current density of 1 amp/ dm^2 .

Composite coating using copper as matrix metal have been produced from sulphate and alkaline cyanide bath. Unlike Ni, Cu gave great difficulty in codeposition. Using copper cyanide solution SiO_2 , Al_2O_3 , SiC could all be deposited with copper very easily. But particles like W, Cr are codeposited more readily from acid solution. Snaith and Grooves (18) studied the codeposition process of SiC, chromium diboride and SiO_2 with Cu from conventional CuSO_4 bath, where zeta potentials and surface charge density played an important role in their process of codeposition. But Malone (19) failed to yield a composite of Cu and $\gamma\text{-Al}_2\text{O}_3$ for acid CuSO_4 bath by using and not using promoters as described by Tomaszewski (20). Like Nickel cermets, copper cermets are also capable of withstand high temperature operation. Cu- Al_2O_3 composite with 6.5% of Al_2O_3 by volume was reported to be unaffected even after

annealing at 600°C and the hardness and tensile strength was twice that of pure copper deposit after heat treatment.

Compared to Cu and Ni, hard matrix of Cu was found to be much more attractive due to its good wear and oxidation properties. Unfortunately the chromium plating process possess very poor cathode current efficiency and micro throwpower. Cobalt metal having hcp structure possess good wear and frictional characteristics. So production of cobalt borides has found many commercial applications. However, due to its relatively low bulk hardness its use for combining abrasive wear is limited. The yield strength of the Co- Al_2O_3 composite coatings was higher than that of pure cobalt coating and it increased with increasing the Al_2O_3 content of the deposit (21). Co- Al_2O_3 composite coatings produced with ultrasonic agitation of the plating bath showed higher yield strength than the composite coating produced conventionally (21,22).

The new researchers endeavoured codepositing second phase particles in the alloy matrix and very few literature is available in this area. T.N. Devrnikova and A.F. Khrionko (23) successfully codeposited boron particles in the Ni-P. matrix. They found that the boron particles had a marked effect on the phosphorous content of such coatings and the rate of deposition of Ni.

Diffusion annealing of Ni-P-B-Coatings lead to the formation of a new phase and an improvement in their physico-mechanical properties, in particular hardness and wear resistance.

2.5 NUCLEAR CONTROL COATINGS:

In the field of radioactive materials,

UO_2 and ThO_2 can be codeposited with Ni to produce a coating which can be used either as an ion detector or as a fuel element. Neutron absorbing materials such as boron and its compounds have been codeposited with Ni to produce reactor coating materials. A new field of growing interest is to include luminescent phosphorous in metal plating which can be used in the decorative field, in name plates and traffic signals.

2.6 HEATTREATABLE METAL ALLOY COATINGS:

Recently the most interesting area of Electro-deposition of composite coating development is that of producing heat treatable coatings and electroforms. Bazzard and Boden (24) have shown that Cr powder can be codeposited with Ni and heat treated to produce Ni-Cr alloy. By this technique coppo-Nickel, stellite, ball bearing steels have been produced. Metal powder and ceramics codeposited simultaneously with Cr and Co-Mo alloy are being developed as high temperature corrosion and oxidation resistant coatings. Also Cu-Ag alloy having a high hardness with 8-14% inclusion of Ag powder has been successfully produced by Faifulline (25). Codeposition of Ni powder in Ni matrix

in electron tubes has been studied by varadi et al.. Such a Ni matrix improves heat and electrical conductivity and minimizes the detrimental effect of high voltage sparking. Cahassaing et al (26) investigated the Ni-Mo and Co-Mo electrodeposits as a function of molybdate concentration in a citrate complex bath.

2.7 MECHANISM OF CODEPOSITION:

Number of possible mechanisms have been proposed by different investigators, but the actual mechanism of codeposition of fine particles in the matrix metal during conventional electroplating is still not clear. These mechanisms can be mainly classified as

- (i) Mechanical entrapment.
- (ii) Electrophoresis.
- (iii) Two stage adsorption mechanism.

2.7.1 MECHANICAL ENTRAPMENT:

The mechanical entrapment can be described as a probability process in which the particles are brought in to contact the electrode by agitation of the plating bath. So if the metal deposition is sufficiently high the particles which will be delayed at the cathode will be trapped by the flux of the depositing metal and eventually engulfed in the deposit. Hence the cathode

efficiency is important for getting codeposition by this mechanism. But during violent agitation of electrolyte, it is quite improbable for a particle to be attached to the cathode surface that long during which metal matrix would grow around to make it stable. Goldthorpe (27) showed that Al_2O_3 can be deposited with Ni-acid bath but not with Cu-acid bath though the cathodic efficiency of copper is 95%. This concluded that the particle entrapment depend upon microthrow power and not on the metal deposition rate. Electrolyte with good microthrowing power would be expected to plate behind the particles and move it away from the cathode along with the growing metal, while one with poor microthrowing power would be expected to build up around and entrap the particles. Also large particles due to its higher gravitational force that promote downward movement. i.e. the cube of its radius and the attractive force due to surface charge, which would be proportional to the square of radius, vary differently depending upon the particle size. So the thought was directed towards the importance of surface charge of particles, by which the codeposition process can be described more clearly.

7.2 ELECTROPHORESIS:

Electrophoresis is a phenomena by which charged particles placed in a liquid move under the influence of applied electric field. The nature of the surface

charge will decide the direction of the particle movement. Positively charged particles will move towards cathode and vice-versa. The velocity of moving particles can be given as

$$V = \frac{DEZ}{4\pi\mu} \dots\dots\dots(1)$$

where,

V = Electrophoretic Velocity

E = Applied Potential gradient

D = Dielectric constant of the medium

Z = Zeta potential

μ = Coefficient of viscosity of the medium.

For particles possessing a zeta potential of + 20mv, moving under a potential gradient of 0.25 V.cm^{-1} the electrophoretic velocity calculated from the above expression is $5 \times 10^{-5} \text{ cm. Sec}^{-1}$. The hydrodynamic transport by agitation is of the order of 5 cm.Sec^{-1} , which is very high compared to the electrophoretic velocity. But once a particle reaches the electric double layer of the cathode, the electrophoretic transport becomes important, because the hydrodynamic transport of particle would in general be parallel to the cathode surface. The voltage drop across the diffusion layer is much higher than in the bulk of the medium because it occurs over a relatively small distance (100-500 μm) and may be sufficient to cause electrophoretic transport of the particle to the cathode.

The measurement of zeta potential helps to explain the difficulty of codeposition of some particles in certain bath and also the effect of addition of promoter in the bath. The electrodeposition of Al_2O_3 by Sykes and Alner (28) on watts Ni-bath and acid copper bath found that the zeta potential is negative so they concluded that the electrophoretic transport of particles would not take place in this.

2.7.3 TWO STAGE ADSORPTION MECHANISM:

The electrophoretic effect could explain the observed dependence on current density but some difficulty would arise as far as the non-linear concentration dependence is concerned. So Guglielmi (29) proposed a mechanism based on two successive adsorption steps. In the first step the particles are loosely adsorbed on the cathode and they are in equilibrium with particles in suspension. The particles are still surrounded by adsorbed ions and solvent molecules. In the second step the adsorbed ions^{and}/solvent molecules break away from the particle so that a strong and irreversible electrochemical adsorption of particles on the cathode take place. Then the particles are engulfed in the depositing metal. The general equation relating the concentration of the embedded particles to its concentration in suspension and electrode overpotential was given as:

$$\frac{C}{\alpha} = \frac{W.i_o}{n.F.d.v_o} \cdot e^{(A-B)\eta\left(\frac{1}{k} + C\right)} \dots(2)$$

where,

C = Concentration of particles in the bath in volume percent

α = Volume fraction of particles in the deposit

W = Atomic weight of the deposited metal

n = Valence of the metal

d = density of the metal

F = Faraday's constant

η = Overpotential

k = Adsorption constant

i_o, A = Constants related to metal deposition

v_o, B = Constants related to particle deposition.

At different values of the over potential, η , if C/α is plotted against C, we obtain a set of straight lines converging at the point where $C = 1/k$,

$$\text{Slope} = \tan \phi = \frac{W.i_o}{n.F.d.v_o} \cdot e^{(A-B)\eta} \dots\dots(3)$$

Equation (2) is derived for a constant potential, but it is approximately valid at constant current, as long as the factor α is small. In this approximation Tafel's equation, given below, relates the over-potential η , to the applied current density, i ,

$$i = i_o e^{A\eta} \quad (4)$$

$$\text{or } A\eta = \ln\left(\frac{i}{i_o}\right) \quad (5)$$

Now

$$\begin{aligned} i_o \cdot e^{(A-B)\eta} &= i_o e^{(1-B/A)A\eta} \\ \text{or} \quad &= i_o e^{(1-\frac{B}{A})\ln\left(\frac{i}{i_o}\right)}, \text{ using eqn (5)} \\ \text{or} \quad &= i_o e^{\ln\left(\frac{i}{i_o}\right) (1-B/A)} \\ \text{or} \quad &= i_o \left(\frac{i}{i_o}\right)^{(1-B/A)} \\ i_o e^{(A-B)\eta} &= i_o^{B/A} \cdot i^{(1-B/A)} \quad (6) \end{aligned}$$

Substituting (6) in (3) and using the logarithms we obtain

$$\log (\tan \phi) = \log \frac{W.(i_o)^{B/A}}{n.f.d.v_o} + (1-B/A) \log i \quad (7)$$

If $\tan \phi$ is plotted against i on logarithmic coordinates a straight line is obtained having a slope equal to $(1-B/A)$ from which the constant B can be evaluated in terms of A .

Guglielmi verified his model by codepositing TiO_2 and SiC particles with nickel from sulphamate baths. The codeposition experiments were carried out at various current densities. The experimental points, as predicted by his model, fall on a set of straight lines converging at a point on the C axis, when C/α was plotted against ' C '. The values of $1/k$ for TiO_2 and SiC were 0.19 and 0.12,

respectively. Celis and Roos (30) also found that this model was valid for codeposition of α - Al_2O_3 with copper from acid copper baths with and without the addition of Tl^+ ions as promoter. The promoter did not change the value of $1/k$ which was equal to 0.35. From this they concluded that the interaction of the particles and the cathode, indicated by the parameter k , did not change upon addition of Tl^+ ions.

The significance of various parameters in the above mechanism is discussed below.

2.7.3.a Significance of the Relative Values of A and B:

Guglielmi (31) showed that with increasing current density the volume fraction of codeposited particles, α , increased in the Ni-SiC system where $B=1.51A$, i.e. $B > A$ and decreased in the Ni- TiO_2 system where $B = 0.65A$, i.e. $B < A$. Celis and Roo's (30) also observed that in the Cu - α - Al_2O_3 system the volume fraction of the codeposited particles increased up to 2 A/dm^2 when $B = 1.53 A$, i.e. $B > A$, but above that current density, it decreased with increasing current density. It was concluded (31) that if $B > A$, i.e. the slope of the straight line given by equation (7) is negative, the volume fraction of codeposited particles would increase with increasing current density, while if $B < A$, i.e. the slope of the straight line given by equation (7) is positive, the

volume fraction of the codeposited particles would decrease with increasing current density.

2.7.3.b Significance of the Adsorption Steps:

The overall kinetics of the process that occurs in consecutive steps are always determined by the slowest step. Attempts have been made by some investigators (31-33) to establish the adsorption step that controls the deposition kinetics, and also the relative rates of the various steps.

Guglielmi and Cerbone (33) argued that, if the rate controlling step during composite plating was the first step of adsorption, i.e. the loose adsorption of particles on the cathode, then the deposition rate of the particles,

$\frac{dV_P}{dt}$, should be independent of the electric field and be proportional to the particle concentration in the bath, C, i.e.

$$\frac{dV_P}{dt} = DC \quad (9)$$

where,

V_P = volume of particles in the deposit

D = constant of proportionality

C = concentration of particles in the bath,
expressed in volume percent

If α is the volume fraction of particles in the coating, then

$$\alpha = \frac{\text{Volume of particles in the deposit}}{\text{Total volume of the deposit}} = \frac{V_P}{V}$$

$$\text{or } V_P = \alpha V$$

$$\text{or } \frac{dV_P}{dt} = \alpha \cdot \frac{dV}{dt} \quad (10)$$

However, the volume of codeposited particles, V_P , is negligible compared to the volume of the metal being deposited V_m . Therefore, the total volume of the composite deposit, V , would be approximately equal to the volume of the metal being deposited, i.e.

$$\text{or } \frac{dV}{dt} = \frac{dV_m}{dt} \quad (11)$$

Substituting equations (10) and (11) in (9) we obtain

$$\alpha \cdot \frac{dV_m}{dt} = D.C \quad (12)$$

From Faraday's laws of electrolysis, we know that

$$V_m = \frac{W_i \cdot t \cdot i}{n \cdot F \cdot d}$$

$$\text{or } \frac{dV_m}{dt} = \frac{W_i \cdot i}{n \cdot F \cdot d} \quad (13)$$

Combining equations (12) and (13) we obtain

$$\frac{i \cdot \alpha \cdot W_i}{n \cdot F \cdot d} = D.C$$

$$\text{or } \frac{\alpha \cdot i}{C} = \frac{D \cdot n \cdot F \cdot d}{W_i} = \text{constant} \quad (14)$$

Therefore, if the first step of adsorption were the rate-controlling step during composite plating, the value of the term $\frac{\alpha_i}{C}$ would not change with current density.

Guglielmi and Cerbon (33) observed that in the case of Ni-Si composite coatings the shape of the plot of volume fraction of particles in the deposit, α , against the volume percent of the particles in the suspension, C , changed with current density. At lower current densities the curve had a characteristic asymptotic shape while at high current densities it was linear. From this they concluded that the rate-controlling steps were different at those two current densities. They also showed that $\frac{\alpha_i}{C}$ tended to become constant at higher current densities. Based on the above arguments, they concluded that at higher current densities, the first step of adsorption, i.e. loose adsorption of particles on the cathode surface, was the rate-controlling step.

For Cu- Al_2O_3 composite coatings, Celis and Roos (30) observed that the amount of codeposited $\alpha\text{-Al}_2\text{O}_3$ particles increased up to 2 A/dm^2 but decreased thereafter with increasing current density. On studying the cathodic polarisation characteristics of the plating bath, they observed that the overvoltage versus current density curve deviated from the

ideal Tafel behaviour above 2 D/dm^2 . This indicated that upto 2 A/dm^2 the deposition kinetics were under charge-transfer overvoltage control, i.e. the second adsorption step was rate-controlling. Above 2 A/dm^2 the first adsorption step controlled the deposition kinetics. This conclusion is supported by the analysis proposed by Guglielmi and Cerbone (33) . By replotting the Celis and Roos data we observe that the $\frac{\alpha i}{C}$ value tends to become constant at current densities higher than 2 A/dm^2 .

The relative rates of the first adsorption step in different composite plating systems were determined by Guglielmi (31) in the following manner. He wrote a slightly modified form of the Langmuir adsorption isotherm:

$$\sigma = \frac{K.C}{1+K.C} \cdot (1-\Theta) \quad (15)$$

where,

σ = loose adsorption coverage

K = adsorption constant, a parameter representing the interaction of the particle and the cathode

C = concentration of the particles in suspension

Θ = strong adsorption coverage

For particles of reasonably regular shape, the volume fraction of the codeposited particles, α , has nearly the same value as the surface fraction or coverage, Θ . It

is therefore possible, knowing K and Θ , to compute the adsorption coverage, σ , using the above equation. The value of σ so calculated would indicate the magnitude of the loose adsorption.

Celis and Roos (30) tried to show that the rate of the second adsorption step can be related to the parameter v_o of equation (12) in the following manner. They observed that up to 2 A/dm^2 the deposition kinetics in $\text{Cu-}\alpha\text{-Al}_2\text{O}_3$ system, with or without Tl^+ ions, were controlled by the second adsorption step. In the presence of Tl^+ ions the volume fraction of the codeposited particles, α , increased as compared to deposition from the conventional bath, and was practically independent of the current density, giving $B = A$. The value of K also remained unchanged upon addition of Tl^+ ions. When $B = A$, equation (12) was reduced to

$$\frac{C}{\alpha} = \frac{W \cdot i_o}{n \cdot F \cdot d \cdot v_o} \cdot \left(\frac{1}{K} + C \right) \quad (16)$$

This indicates that at different current densities a set of straight lines would reduce to a single straight line. In the above equation the parameters W , i_o , n , F and D are related to the metal deposition. Therefore, for a given metal plating bath, at any given C , α will depend on v_o and K . Since the Tl^+ ions are neither adsorbed on the Al_2O_3 particle surface nor discharged at the cathode, and

the value of K remains unaltered, it was considered that the increase in α was due to the acceleration of the second adsorption step by Tl^+ ions. It was therefore concluded that the rate of the second adsorption step was related to the parameter v_0 .

It was indicated that reduction of metallic ions adsorbed on the particle occurs during the second adsorption step. Increasing the current density increases the rate of reduction and would, therefore, be expected to increase the rate of the second adsorption step. Therefore, above a certain current density, we could expect that the second adsorption step would be faster than the first adsorption step, and that the deposition kinetics would then be controlled by the first adsorption step. In composite-plating systems, where the deposition kinetics are controlled by the second adsorption step but there are different rates of the first adsorption step, the term $\frac{\alpha i}{C}$ would be expected to increase with current density, i . However, the rate of increase of $\frac{\alpha i}{C}$ with i may be expected to increase in a system where the first adsorption step is relatively faster. In a system where the first adsorption step is relatively slow the rate of increase of $\frac{\alpha i}{C}$ with i would be expected to decrease.

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CHAPTER III

EXPERIMENTAL SETUP AND PROCEDURE

3.1 MATERIALS:

The following materials were used for the experiments ,

- (i) Chromium trioxide, L.R. Grade, Glaxo Lab., Bombay.
- (ii) Sulphuric Acid, G.R. Grade, Sarabhai Chem., Baroda.
- (iii) Nitric acid, G.R. Grade, Sarabhai Chem., Baroda.
- (iv) Formaldehyde, L.R. Grade, Glaxo Lab., Bombay.
- (v) Tungsten Carbide Power Particle Size 1-5 μm .
- (vi) Anode material 10% Sn - Pb alloy.
- (vii) Cathode, Mild Steel, (4.0 x 1.0 x 0.1 cm^3).

3.2 EQUIPMENTS:

- (i) Regular D.C. Power Supply, Networks, NPS 100.
- (ii) Magnetic Stirrer.
- (iii) Heating element connected to the relay unit through Variac.

The cell (A beaker of 400 ml capacity) with the stirring element was placed on a heating element which rest on the platform of a magnetic stirrer cum hot-plate. A round asbestos sheet was placed in between the platform and the heating element to minimise, the thermal

loss. The top of the cell was covered with a lid containing provisions for the introduction of the electrodes into the bath containing electroplating solution and tungsten carbide.

The electrical power to the heating element was supplied through an on/off relay control. The two leads of the Beckmann thermometer were also connected to the on/off relay control. The desired temperature of the bath was achieved by keeping the indicator which moves over a temperature scale, at the desired temperature. The indicator moves upwards or downwards on the scale according to the rotating direction of the head attached to the indicator.

3.3. ELECTROPLATING SOLUTION:

Composition of the hexavalent chromium electroplating bath is given in table 1. The ratio of H_2SO_4 acid to chromic acid was maintained at 1:100 for all the experiments.

3.4 SPECIMEN PREPARATION:

Mild steel flat specimens were used as cathode. They were polished on an endless emery belt. Water was used as the lubricant to hasten the polishing action and to decrease the drastic heating of the specimens during polishing. After polishing in the emery belt, the specimens were polished on emery papers up to 4/0 to get a mirror like surface

on both sides. All the sharp corners and edges of the specimens were rounded off to avoid dendritic deposition at these places.

3.5 EXPERIMENTAL PROCEDURE:

The experimental setup used for the present study is given in the schematic diagram (Fig. 3.1). 400 ml of the bath solution was transferred to the electrolytic cell. The solution was stirred at a speed of 500 rpm. Weighed amount of we powder was added to the bath little by little. The temperature was kept constant using constant temperature bath with Beckmann thermometer and on/off relay control. The solution containing WC was blended for three hours unless otherwise stated, to ensure good wettability and uniform distribution of powder particles in the bath. When the required temperature and blending time were achieved, the electrodes were lowered, and it was connected to the DC power supply. Plating time was 3 hours. Distilled water was added to make up for the evaporation losses .

3.6 ANALYSIS OF COATINGS:

Chemical analysis was used to find the cathodic efficiency and weight % of WC in the coatings. The weighed specimen before and after the deposition was dipped in dilute sulphuric acid (20%) containing formaldehyde(4CC/Lit).

After all the coating were dissolved, the solution was further diluted and the weight of WC particles were determined gravimetrically.

Weight of sample before plating $= W_1$

Weight of sample after plating $= W_2$

Weight of WC in the coating $= W_3$

Plating time $= t$ Sec.

Current density $= i$ A/dm²

Area of cathode $= A$ dm²

$$\text{Cathodic efficiency} = \frac{i \cdot t \cdot 52.0 \cdot A \cdot (W_2 - (W_1 + W_3)) \cdot 100}{(96500.0) \cdot 6}$$

$$\text{Weight \% of WC} = \left(\frac{W_3}{W_2 - W_1} \right) \cdot 100\%$$

α = Volume fraction of WC in the coating

C = Volume percentage of WC in the bath

d_{WC} = Density of WC

d_{Cr} = Density of Cr

$$\alpha = \frac{1}{\left(1 + \frac{d_{WC}}{d_{Cr}} \right) \left(\frac{W_2 - (W_3 + W_1)}{W_3} \right)}$$

$$C = \frac{\text{Bath load}}{10 \cdot d_{WC}} \%$$

TABLE 3.1COMPOSITION OF CHROMIC ACID BATH USED IN THE PRESENT STUDY

CHROMIC ACID	240 g/l.
SULPHRIC ACID	2.4 g/l
TEMPERATURE	55°C
CURRENT DENSITY	55 A/dm ²

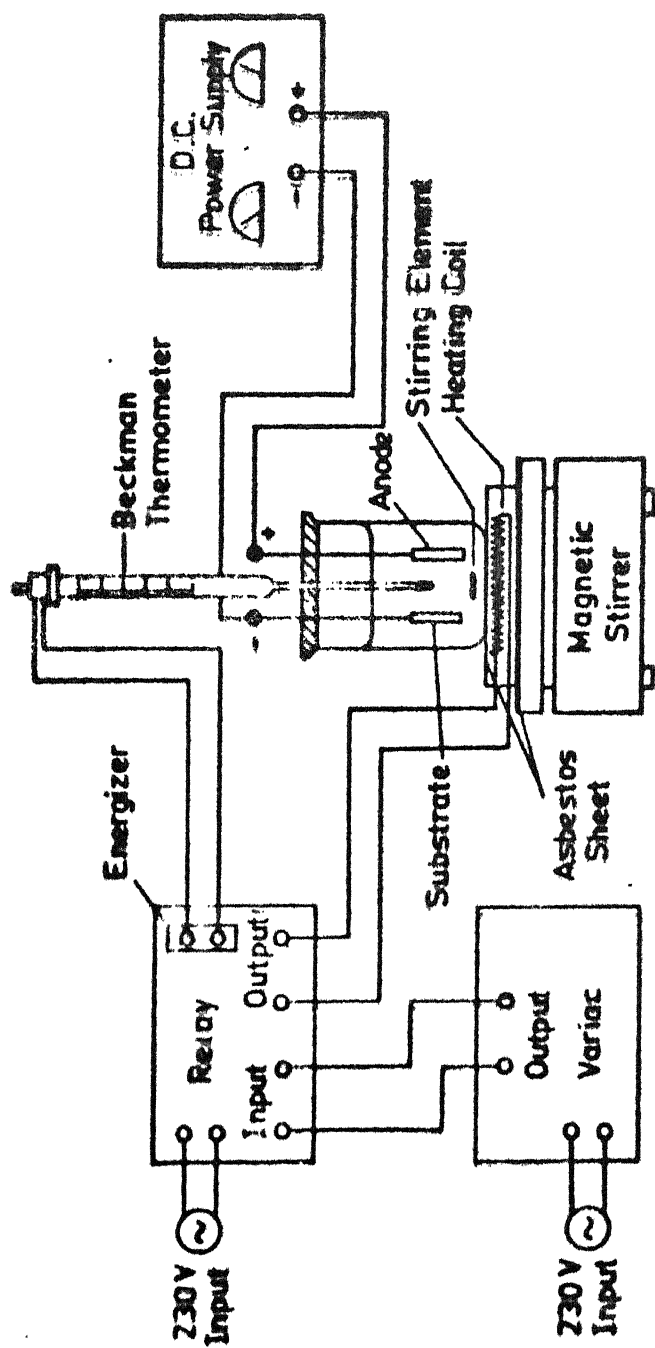


Fig.3.1 Schematic diagram of experimental setup for electro-deposition of CF-WC composite coatings.

CHAPTER IV

RESULT AND DISCUSSION

4.1 RESULTS:

The effects of the following variables were studied for the codeposition of tungsten carbide (WC) with chromium from hexavalent chromic acid bath. The plating period for all the experiments were three hours. The specimen size was $4.0 \times 1 \times 0.1 \text{ cm}^3$.

4.1.1 Effect of Chromic Acid Concentration in the Bath:

The effect of chromic acid concentration in the bath on the amount of WC codeposited with chromium was studied at a sulphuric acid to chromic acid ratio of 1:100, bath temperature 55°C , current density 55 A/dm^2 and the bath load of 90 g/l WC . At low concentration of chromic acid no codeposition of tungsten carbide occurred. Maximum codeposition occurs at a chromic acid concentration of 240 g/l , above this concentration the amount of WC codeposited with Cr decreased slightly with increasing chromic acid concentration. Fig. 4.1 . Further work was carried out at a chromic acid concentration of 240 g/l .

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4.1.2 Effect of Blending Time:

The blending time was varied for 30 to 240 minutes, and its effect on weight percentage of tungsten carbide in the coating (WTP) was found at constant current density, temperature and concentration of chromic acid (55.0 A/dm^2 , 55°C and 240 g/l). The rate of weight percentage of WC in the coating increases with increase in time up to 240 minutes and above this time the rate was very slow. From this experiment it was observed that the optimum blending time to get maximum WTP was three hours. All further works were carried out by blending the WC in the bath for three hours with constant stirring so that all the 'WC' particles got wetted and remain in uniform suspension Fig. 4.2.

4.1.3 Effect of Bath Temperature:

The effect of bath temperature on 'WTP' was studied at different bath loads. The current density and chromic acid concentration being 55 A/dm^2 and 240 g/l respectively. At all bath loads, increase in temperature upto 55°C increases the WTP in the coating, beyond which temperature has practically no effect (Fig. 4.3) . Further tests were therefore carried out at 55°C .

4.1.4 Cathode Current Efficiency:

The cathode current efficiency (CCE) was calculated under different plating condition such as temperature, current density and bath load. From Fig. 4.4 it can be seen that, the increase in the bath load has no effect on CCE, The increase in temperature increases the CCE upto 55°C , beyond that temperature has practically no effect Fig. 4.5. The same trend was observed by increasing current density, here the CCE remained constant above 55 A/dm^2 Fig. 4.6.

4.2 DISCUSSIONS:

If the two stage adsorption mechanism proposed by Guglielmi be applicable to any composite plating system, plotting C/α against C for different values of current density or temperature should give a set of straight lines converging at a point where $C=1/k$. (2-5).

On plotting C/α against C at different temperatures, for ^{the} present investigation we obtain a set of straight lines converging at a point where $1/k = -0.36$ (Fig. 4.8). Although there is some scatter in the results, especially at low temperatures, it seems reasonable to conclude that the two stage mechanism proposed by Guglielmi is also applicable in the present Cr-WC system at different

temperatures at 50 A/dm².

After establishing the validity of the two step adsorption mechanism in Cr-WC system, attempts have been made to determine the rate controlling adsorption step in the system by studying the effect of different plating variables on the amount of codeposited particles at 55°C. The volume fraction of codeposited particles in the coating, α , was plotted against the volume percentage of particles in the bath, C, at different current densities. The resulting curve had the characteristic asymptotic shape (Fig. 4.9) indicating that at all current densities studied at 55°C the deposition kinetics were under the control of same adsorption step. On plotting $\frac{\alpha i}{C}$ against current density, i , we observe that the term $\frac{\alpha i}{C}$ does not tend to become constant but keeps on increasing at all current densities at different volume percentage of particles in the bath (Fig. 4.10). This as discussed earlier (6), indicates that the deposition kinetics is controlled by the second adsorption step.

Plotting C/α versus C at different current densities at 55°C yields a straight line (Fig. 4.7). This indicates that the two step adsorption mechanism is also valid under these conditions. However, a single straight line is obtained instead of a set of straight

lines. This would mean that under these conditions $B = A$. It was discussed earlier that when the second step controls the deposition kinetics and $B = A$, then the amount of particle codeposited, α , would be independent of current density. Our experimental results confirm this conclusion (Fig. 4.11).

From Fig. 4.3 it can be seen that the amount of tungsten carbide codeposited with chromium increases with increasing temperature upto about 55°C , and there after it was practically independent of temperature. The Tafel relationship shows that both temperature and current density affect overpotential and, therefore, the amount of codeposited particles in the coating in the same way. Thus these would indicate that upto 55°C $B > A$ and at 55°C and beyond , $B = A$.

At low concentrations of chromic acid, e.g. 140 g/l, practically no codeposition of tungsten carbide particles takes place (table 3.1) and C/α becomes infinity. Assuming Gulglielmis two step adsorption mechanism to be valid in this case, it follows that in Eqn (1) C/α can become infinity only if either i_0 or η is equal to infinity or the parameter v_0 or k is equal to zero. The parameters i_0 and η are related to the metal deposition, and since the cathode efficiency of the plating bath remains practically constant with the

decrease in chromic acid concentration in the bath

Table - 4.1, it would appear that the parameters i_0 and η do not become infinity on decreasing the concentration of chromic acid in the plating bath. Decreasing the chromic acid concentration in the bath decreases the amount of chromium ions available to be adsorbed on the tungsten carbide particle and their subsequent reduction. The parameter v_0 , which is related to the rate of reduction of these adsorbed ions, can become zero if no adsorption of chromium ions take place on the tungsten carbide particles. On the other hand, if adsorption of these ions take place, but is not sufficient to bring about any interaction of these particles with the cathode, then k may become equal to zero. It can, therefore, be concluded that by decreasing the chromic acid in the bath either the parameter v_0 or k becomes equal to zero.

CHAPTER - V

CONCLUSIONS

1. It is possible to produce a composite coating of Cr-WC by electrodeposition without any promoter.
2. The amount of WC in the coatings increases with increasing WC content of the bath at all temperature and current density. The optimum WC in the bath was found to be 90 g/l .
3. Current density have no effect on the volume fraction of WC on the coatings.
4. The amount of WC in the coating increases with increasing the temperature upto 55°C and above 55°C temperature has practically no effect.
5. Codeposition of WC would not occur if the chromic acid concentration in the bath is below 140 g/l.
6. The optimum blending time to get maximum codeposition was found to be about three hours.
7. Cathode current density increased with increasing current density upto 55 A/dm² beyond which it remains practically constant at about 18.1%.
8. The Guglielmi's two stage adsorption mechanism was found to be valid for this system and the second stage of adsorption controlled the deposition kinetics.

Table 3.1 Effect of chromic acid concentration on the amount of WC in the coatings at 55°C 55 A/dm² and a bath load of 90 g/l.

Chromic acid concentration g/l.	Cathode current efficiency	Wt% of WC in the coating
140	18.10	0.00
160	17.81	0.80
180	17.70	1.01
200	17.91	1.54
220	18.00	1.68
240	18.20	1.84
260	17.73	1.80
280	18.09	1.74
300	17.87	1.76

Table 4.1 Effect of Temperature and Bath Load on Cathode
Current Efficiency at 55 A/dm².

Bath load g/l	25	40	55	70	90	110
Temperature °C						
35	14.32	14.40	14.38	14.39	14.33	14.31
40	14.82	14.84	14.80	14.83	14.78	14.87
45	15.65	15.64	15.60	15.69	15.63	15.70
50	16.71	16.77	16.75	16.73	16.79	16.74
55	17.98	17.96	18.00	17.83	17.91	17.66
60	18.13	18.10	18.19	18.01	18.09	18.15

le 4.2 Effect of Temperature and Bath load on Amount of WC in the Coating (Wt%) at 55 A/dm².

Bath load g/l	25	40	55	70	90	110
Temperature °C						
35	0.32	0.44	0.62	0.68	0.69	0.69
40	0.50	0.70	0.82	0.85	0.93	0.94
45	0.63	0.90	1.10	1.26	1.35	1.36
50	0.80	1.08	1.30	1.47	1.61	1.36
55	0.89	1.23	1.42	1.60	1.79	1.80
60	0.90	1.23	1.44	1.61	1.80	1.82

Table 4.3 Effect of Current Density and Bath load on Cathod
Current Efficiency at 55°C .

Bath load g/l	25	40	55	70	90	110
Current Density A/dm ²						
30	12.59	12.54	12.46	12.63	12.55	12.58
35	12.90	12.95	12.87	12.84	12.95	12.91
40	13.82	13.86	13.78	13.89	13.84	13.76
45	15.49	15.40	15.56	15.45	15.47	15.80
50	17.50	17.82	17.57	17.86	17.49	17.61
55	17.98	17.96	18.00	17.83	17.91	17.99
60	18.01	18.10	17.90	17.98	18.32	18.28

Table 4.4 Effect of Current Density and Bath Load on Wt%
oc WC in the Coating at 55°C.

Bath load g/l	25	40	55	70	90	110
Current Density A/dm ²						
30	0.80	1.29	1.34	1.50	1.80	1.81
35	0.83	1.25	1.30	1.55	1.79	1.84
40	0.86	1.14	1.49	1.54	1.70	1.77
45	0.85	1.09	1.33	1.58	1.78	1.79
50	0.87	1.21	1.39	1.57	1.74	1.77
55	0.89	1.23	1.42	1.60	1.79	1.80
60	0.89	1.23	1.42	1.61	1.82	1.83

Table 4.5 Effect of Bath Load and Current Density on
Microhardness as Plated.

Current Density A/dm ²	Bath load g/l					
	25	40	55	70	90	110
30	508	545	563	617	669	676
35	574	591	627	662	703	709
40	628	632	671	688	717	719
45	659	679	705	706	733	739
50	681	712	725	734	735	769
55	697	694	738	760	768	809
60	686	743	757	789	842	849

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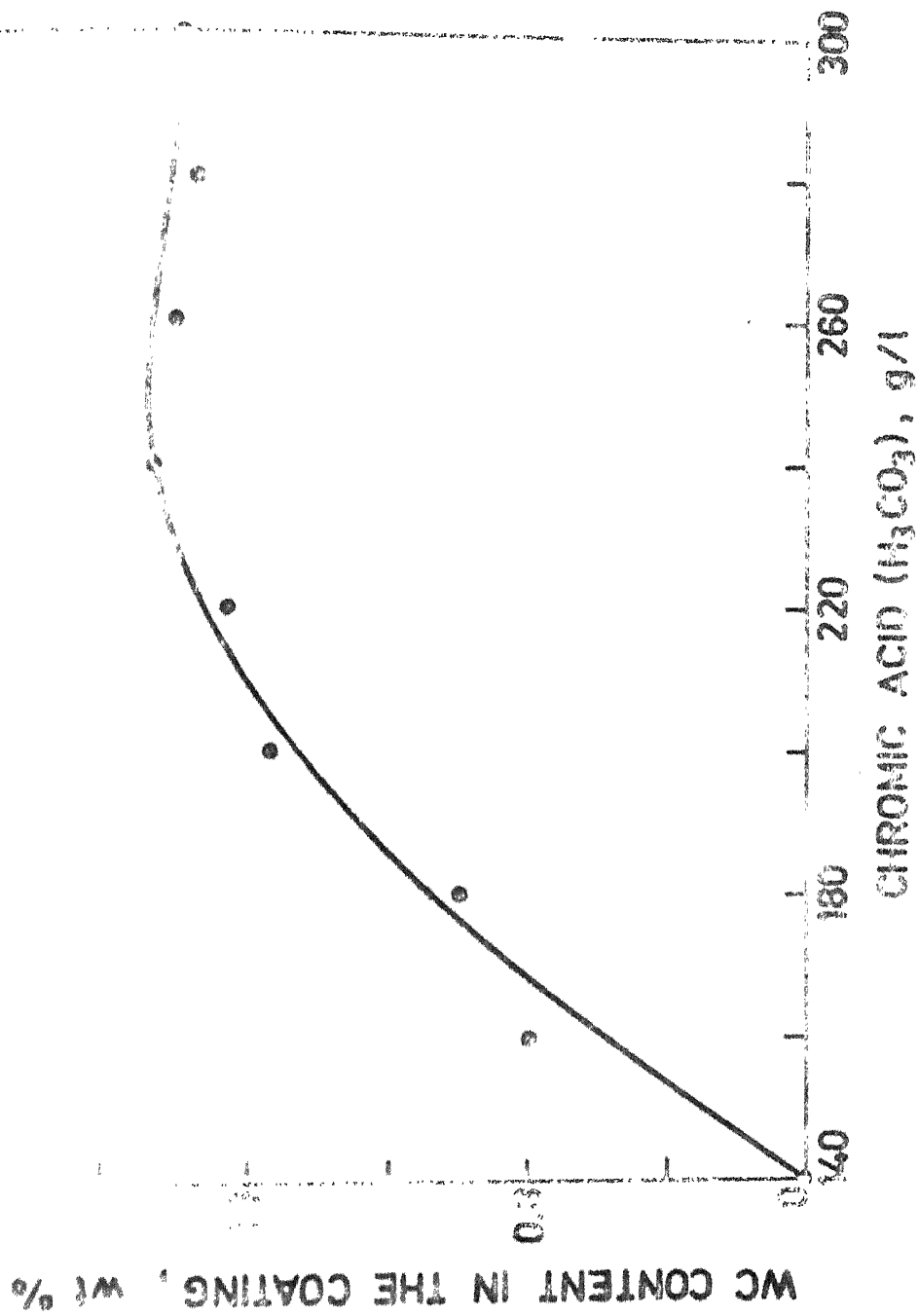


FIG. 4.1 EFFECT OF CHROMIC ACID CONCENTRATION ON THE AMOUNT OF WC ON THE COATING AT 55°C AND 55A/dm² WITH A LOAD OF 50 g/l.

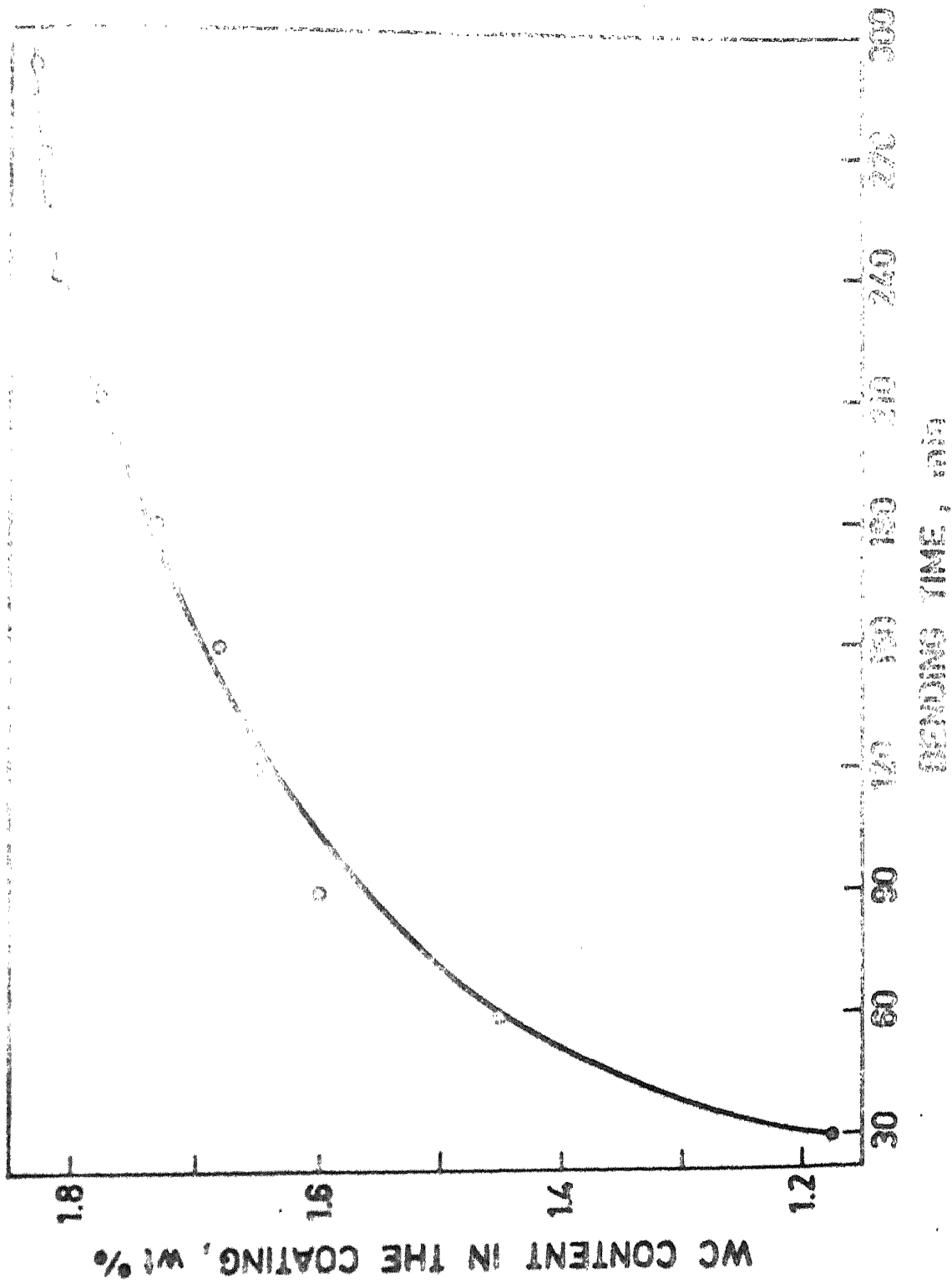


FIG. 4.2 EFFECT OF BENDING TIME ON THE AMOUNT OF WC CONCENTRATED WITH Cr AT 55A/dm², 65°C AND WC CONTENT IN THE COATING

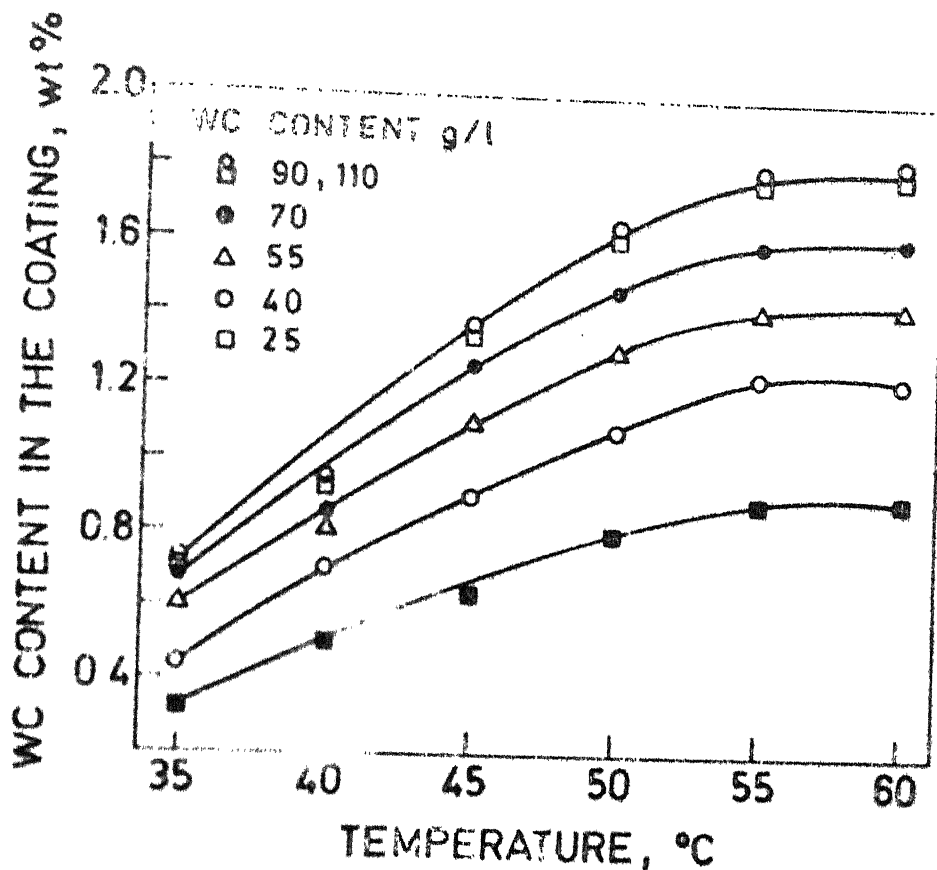


FIG. 4.3 EFFECT OF PLATING BATH TEMPERATURE ON THE WC CONTENT IN CHROMIUM COATING AT 55A/dm² AND DIFFERENT WC CONTENT IN THE BATH.

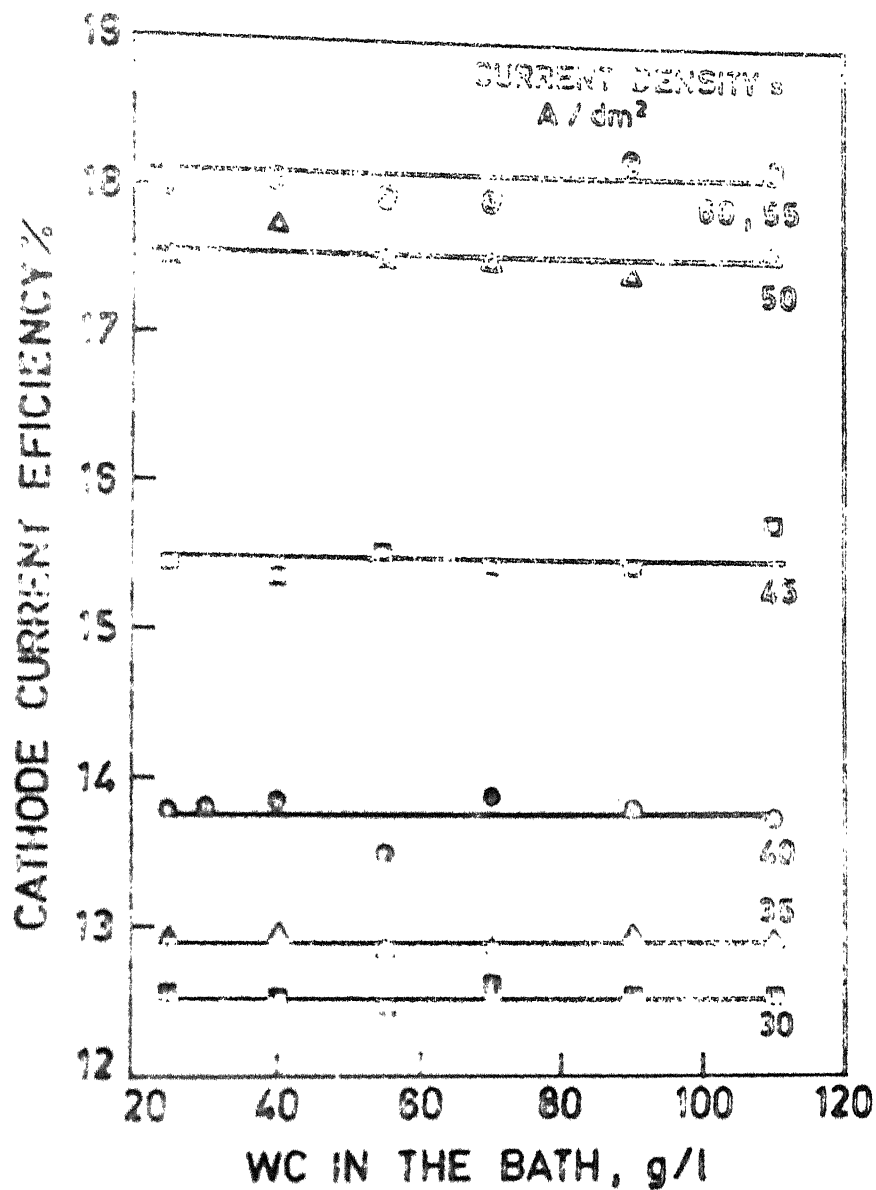


FIG. 4.4 VARIATION OF CATHODE CURRENT EFFICIENCY WITH BATH LOAD AT DIFFERENT CURRENT DENSITY AND A TEMPERATURE OF 55°C.

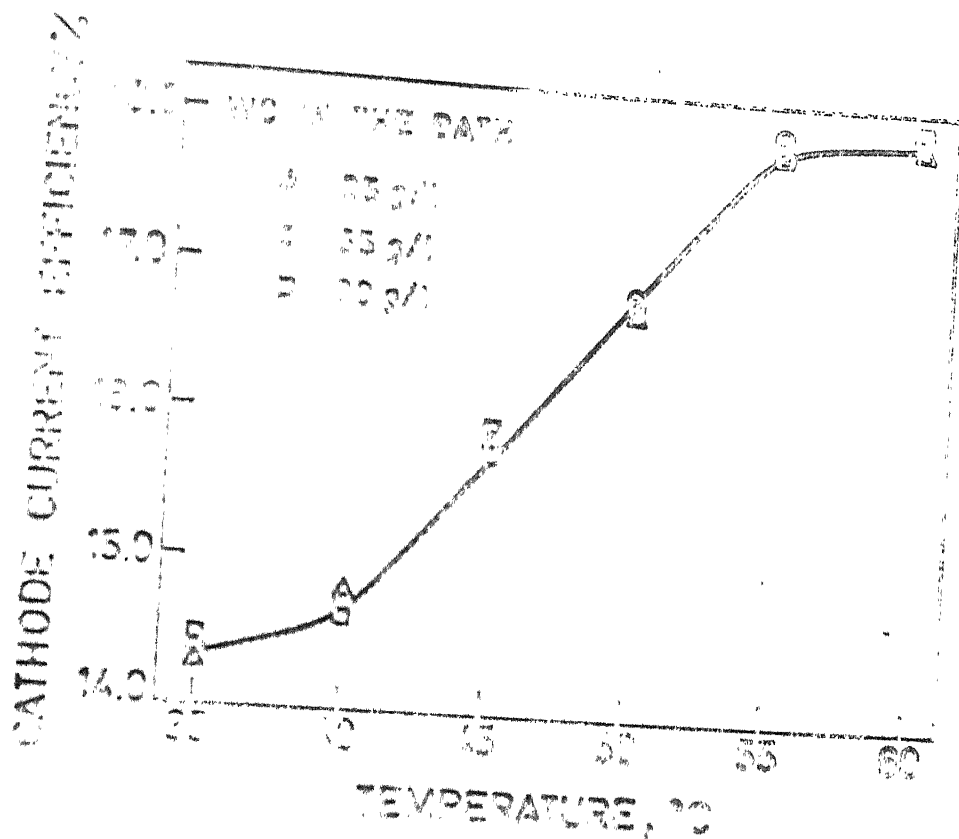


FIG. 4.5 VARIATION OF CATHODE EFFICIENCY WITH TEMPERATURE AT 55 A/dm² AND DIFFERENT WC CONTENTS IN THE BATH.

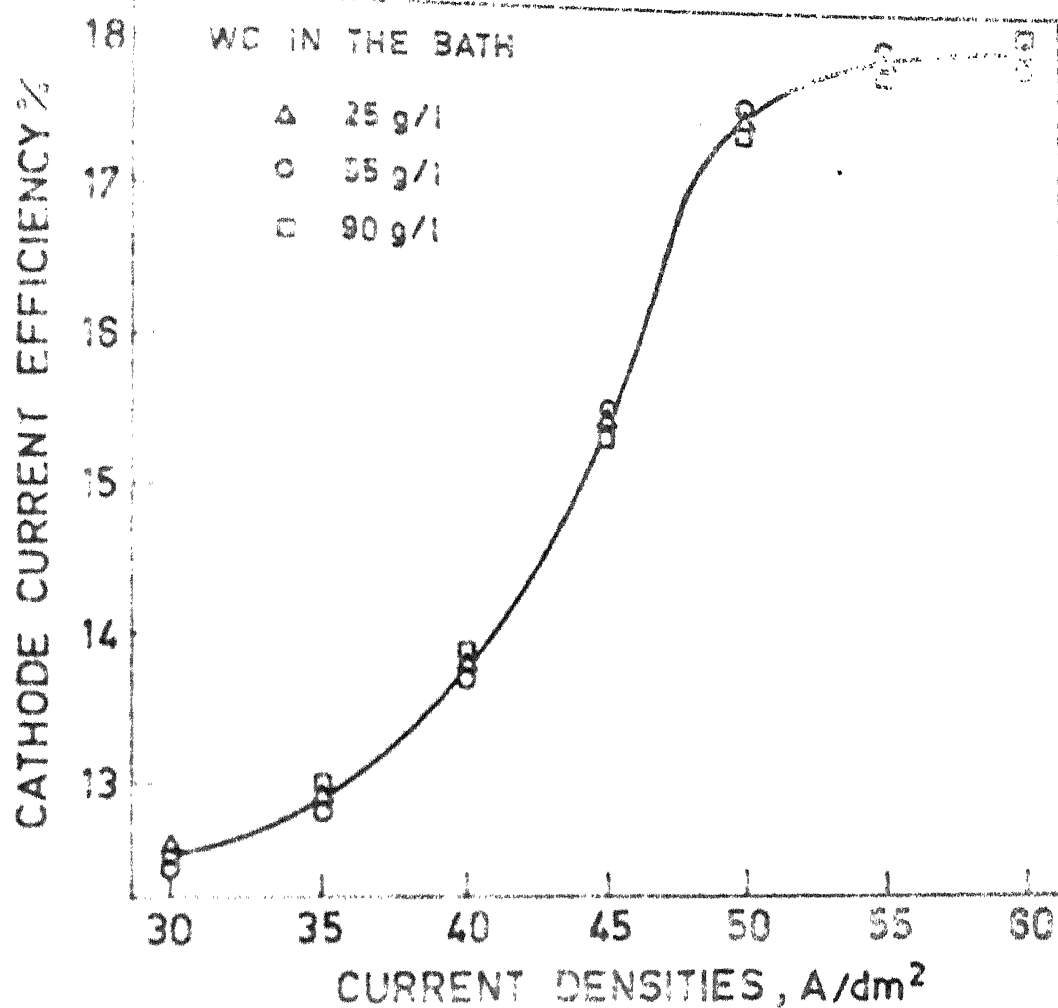


FIG. 4.6 VARIATION OF CATHODE CURRENT EFFICIENCY WITH CURRENT DENSITY AT 55°C AND DIFFERENT WC CONTENT IN THE BATH.

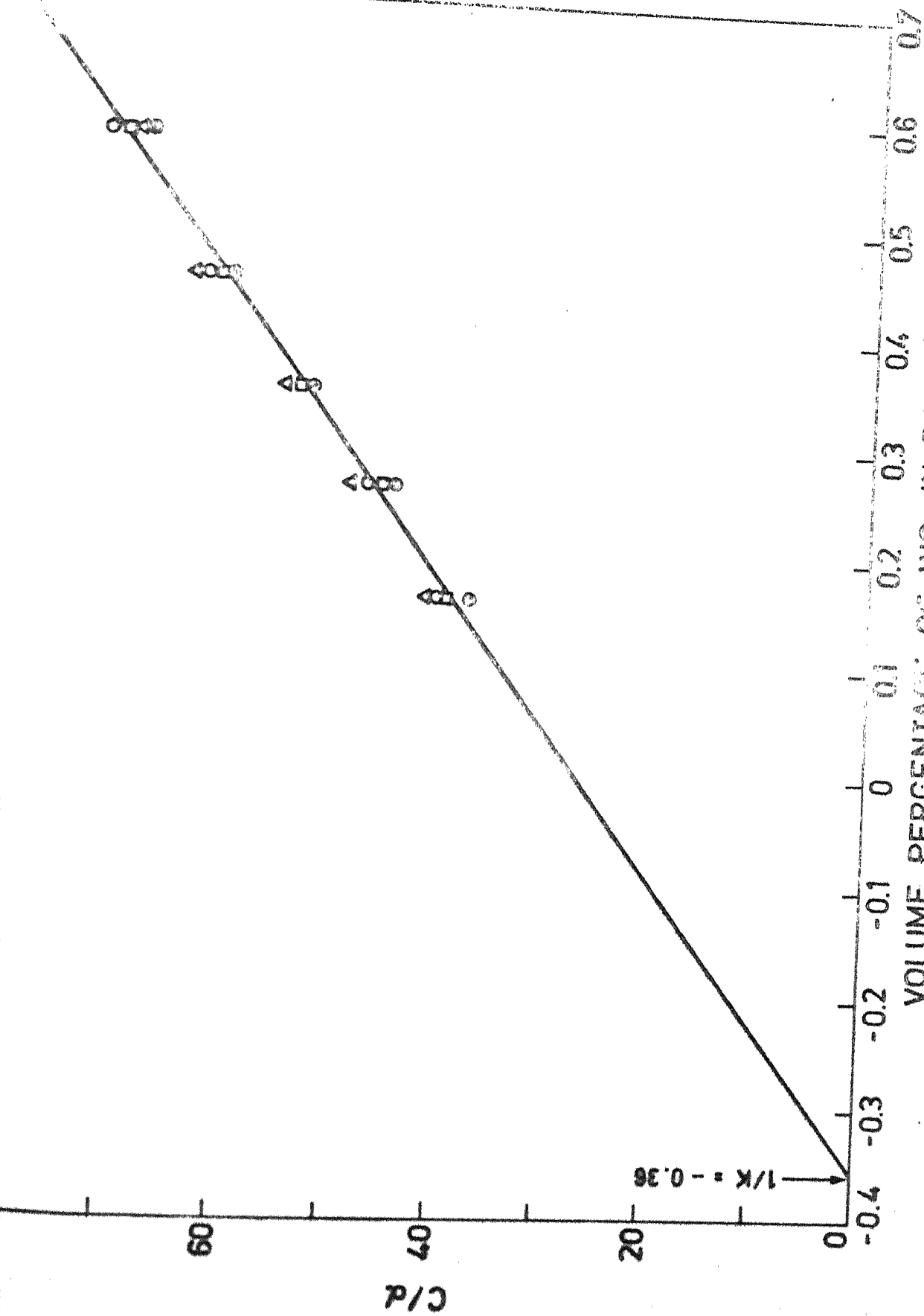
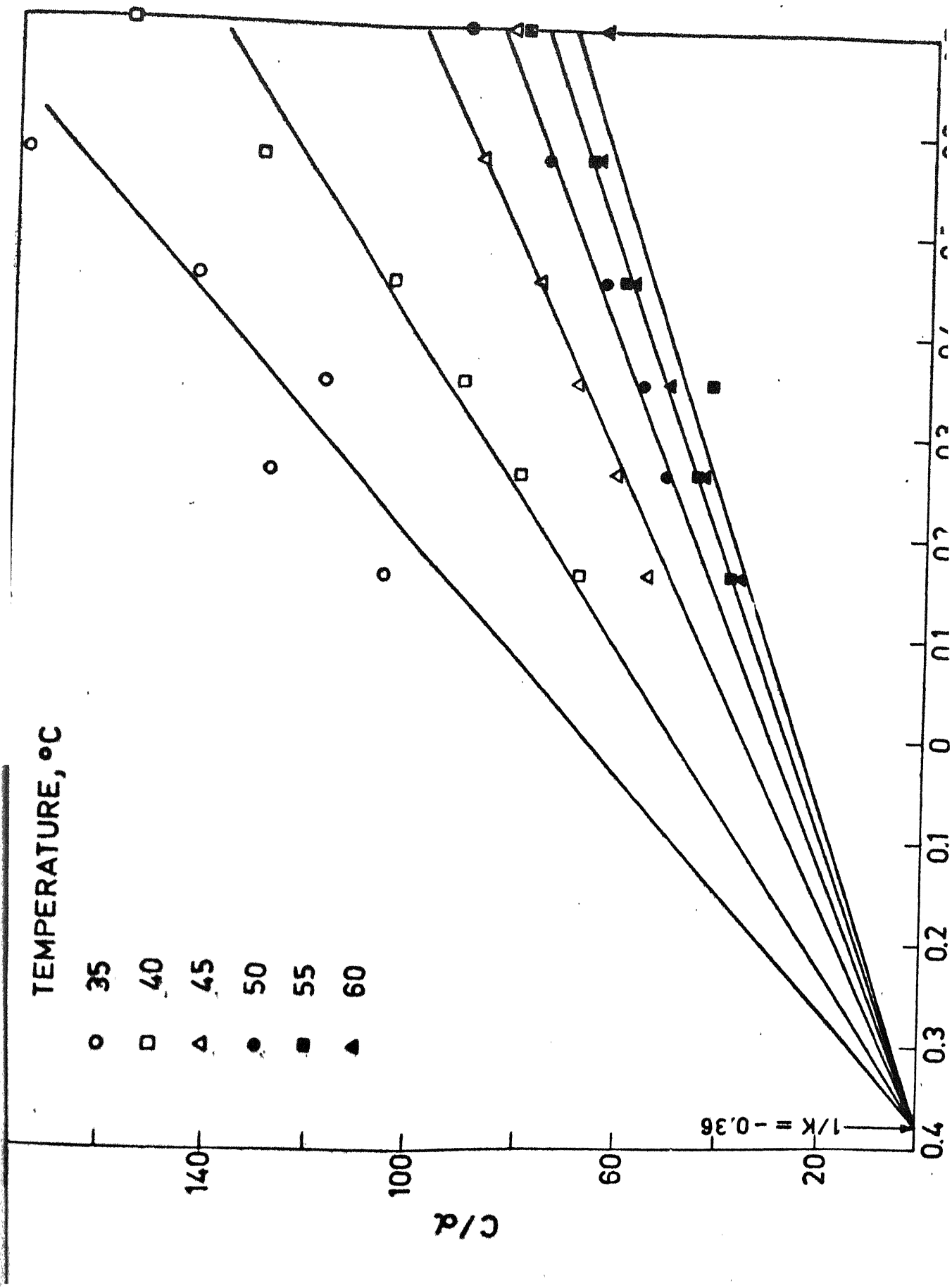


FIG. 4.7 VARIATION OF PARAMETER C/α WITH C AT DIFFERENT CURRENT DENSITIES AT 55°C



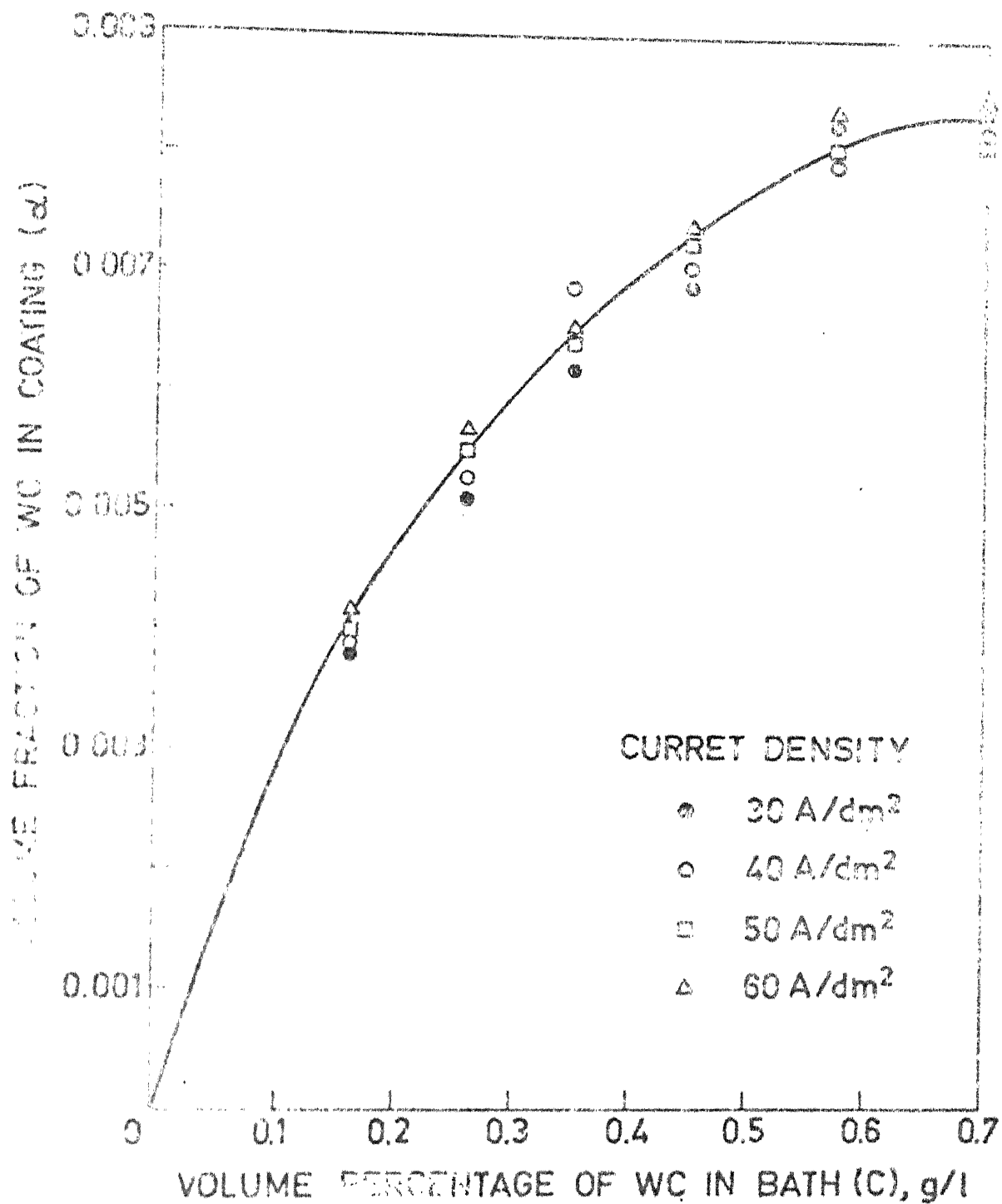


FIG 4.9 VARIATION OF PARAMETER α WITH C AT DIFFERENT CURRENT DENSITIES AT 55°C.

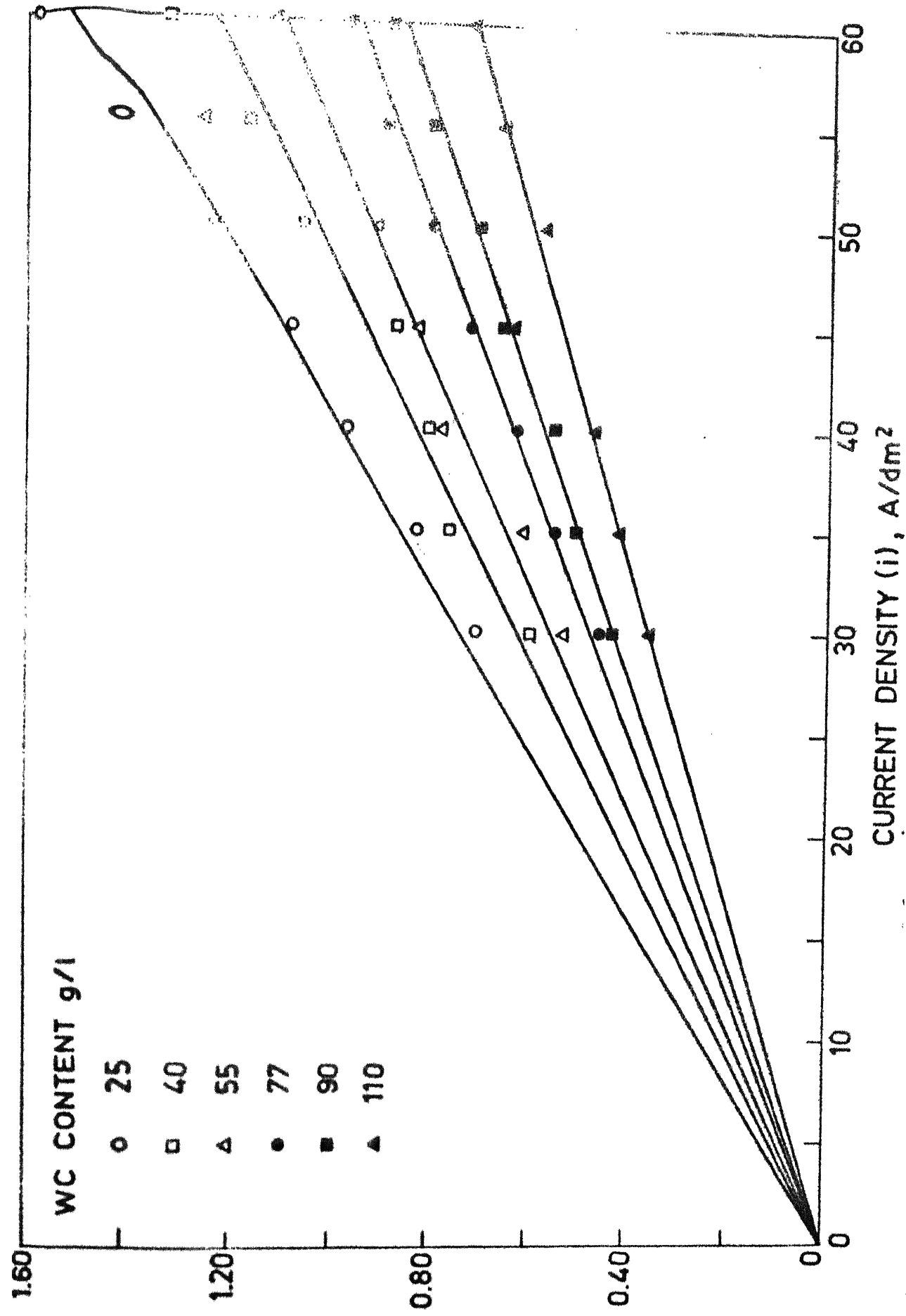


FIG. 4.10 VARIATION OF PARAMETER $\alpha i/c$ WITH i AT DIFFERENT WC CONTENTS IN

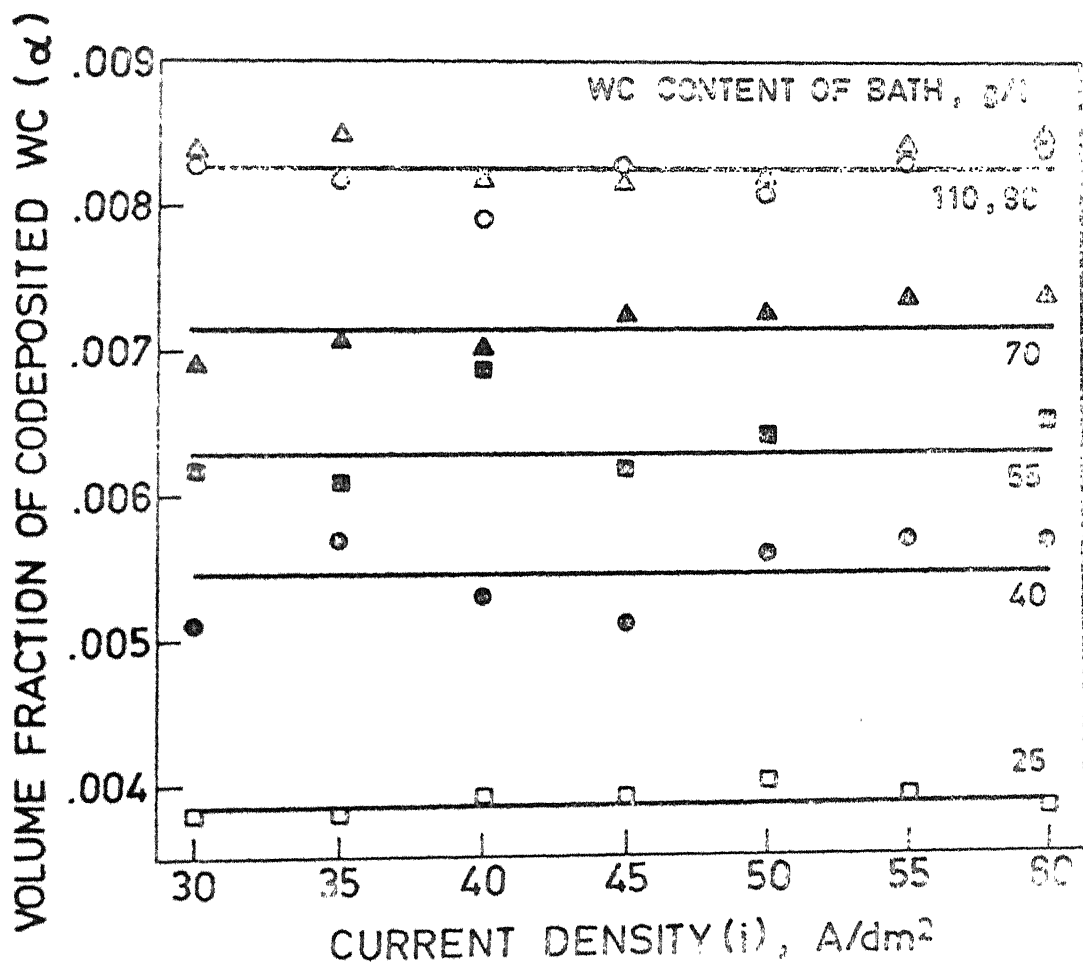


FIG. 4.11 EFFECT OF CURRENT DENSITY ON THE VOLUME FRACTION OF THE CODEPOSITED WC PARTICLES AT 55°C AND DIFFERENT WC CONTENT IN THE BATH.

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